# Trinuclear and Tetranuclear Magnesium Alkoxide Clusters as Highly Active Initiators for Ring-Opening Polymerization of L-Lactide

Yuan Gao, Zhongran Dai, Jinjin Zhang, Xinxian Ma, Ning Tang, and Jincai Wu*

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China

Ⓢ *Supporting Information*

ABSTRACT: Trinuclear and tetranuclear magnesium alkoxide clusters supported by bulky phenolates with triangular or rhombic structures were readily synthesized in acceptable yields via the reaction of 2-*N,N*-dimethylaminoethanol/ methoxyethanol, different phenols, and dibutylmagnesium. These complexes have been characterized using ^{1}H and ^{13}C NMR, elemental analyses, and X-ray crystallography. The experimental results indicate that these clusters are efficient and excellent initiators for the ring-opening polymerizations (ROPs) of L-lactide (LA) and afford polylactides with desired molecular weights and narrow polydispersity indexes (PDIs). Complex **2** can even catalyze the ROP of 4000 equiv of L-lactide in 1 min in a controlled model. Kinetic studies indicate that the polymerization is first-order for both the trinuclear magnesium complex **3** and LA. However, for the tetranuclear magnesium complex **5**, the polymerization rate is first order for **5** and second order for LA.
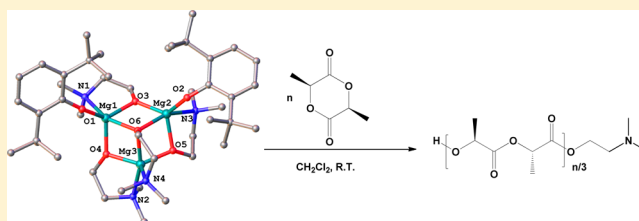
■ INTRODUCTION

Considerable attention has been devoted to polylactic acid in recent years, because of its wide range of applications in the biomedical, packaging, and agricultural fields, since it is a renewable resource and readily biodegradable.[1] The conventional method for synthesizing polylactide (PLA) is the ring-opening polymerization (ROP) of lactide, which results in a well-controlled molecular weight and low polydispersity (PDI).[2] Many complexes including aluminum,[3] titanium,[4] zinc,[5] magnesium,[6] tin,[7] lanthanides,[8] and other metals[9] have been reported as excellent initiators/catalysts for the controlled ROP of lactides to afford polymers with both high and controlled molecular weights. Among these complexes, magnesium alkoxides have attracted considerable attention, because of their nontoxicity and high activity.[10] Undesirable side reactions, such as backbiting and trans-esterification, can be minimized with a sterically encumbered ligand.[11] Despite these advantages, the requirement of delicate, complicated supporting ligands leads to a high cost for the synthesis, limiting its practical value. Therefore, some highly active magnesium initiator/catalyst for the ROP of lactide with simply synthesized ligands have recently been reported to address this issue.[12]

Herein, a series of facilely synthesized trinuclear and tetranuclear magnesium alkoxide clusters bearing bulky simple monophenols as well as their performance in the ROP of lactide are reported. The results indicate that these magnesium alkoxides are highly active for the ROP of lactide under controlled models.

The method for synthesizing multinuclear magnesium alkoxide clusters described herein is also interesting and

valuable. Magnesium alkoxides usually tend to oligomerize via intermolecular O—Mg donor–acceptor bonds. Ashby et al. noted that the thermodynamically preferred solution composition of alkyl magnesium alkoxides correlates with the steric bulk of the alkoxy group and the coordinating ability of the solvent. In coordinating solvents, such as ether and tetrahydrofuran (THF), alkylmagnesium alkoxides can form dimeric solvates, while applying benzene or toluene as solvent leads to unsolvated cubic tetramers for bulky alkoxy groups such as *tert*-butoxy and isopropoxy, but the less-bulky *n*-propoxy group causes the formation of oligomers[13] (Chart 1). Driess et al. also reported that in a low coordinating solvent (i.e., toluene), reactions between different ratios of bulky alkanol and dimethyl magnesium afforded methyl alkoxide magnesium clusters with concurrent biscubic structure in yields of 74%−96%[14] (Chart 1).

To avoid the different structures of magnesium alkoxides in noncoordinating or coordinating solvents, we use the bidentated 2-*N,N*-dimethylaminoethanol/methoxyethanol as the alcohol and introduce a bulky phenoxy into the system to inhibit the dissociation and aggregation reactions. Thermodynamically stable magnesium alkoxides are anticipated in both the coordinating and noncoordinating solvents. The experimental results indicate that this method is suitable for the synthesis of magnesium alkoxides with acceptable yields, and a series of novel trinuclear magnesium alkoxide clusters with triangular structures and tetranuclear magnesium alkoxide

Chart 1. Key Structures of the Magnesium Alkoxides

Dimer   Cubic tetramers   Biscubic structure

Trimers in this work   Tetramers in this work
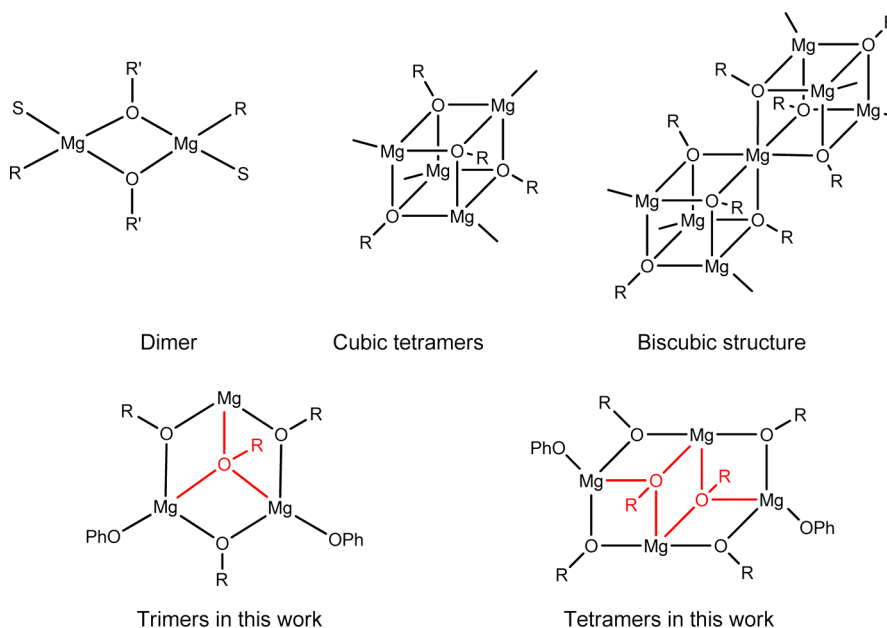
clusters with rhombic structures are reported in this work (Chart 1).

RESULTS AND DISCUSSION

Synthesis and Structures. The reaction of 2,6-di-*tert*-butylphenol (HL₁):DMEA (2-*N,N*-dimethylaminoethanol):Mg^{n}Bu₂ in toluene at room temperature with a ratio of 1:1:1 for the initially designed product shown in Chart 2

Chart 2. Initially Designed Structure (Unsuccessful)
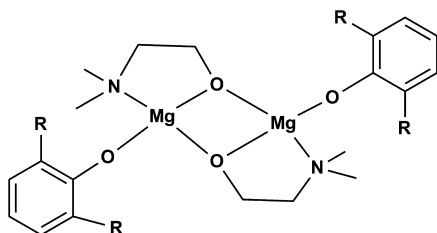
yielded a mixture evidenced by the complicated NMR spectrum. Although a single crystal of complex **1** was obtained from the mixture by recrystallization, the purification of complex **1** is difficult. While heating the reaction mixture up to 60 °C for another 24 h, pure complex **2** can be obtained after recrystallization with an acceptable yield of 52%, which suggests that trimetallic complex **2** is the thermodynamically preferred complex (Scheme 1). The exclusive formation of trimetallic complex **2** is readily achieved by altering the reagent ratio of HL₁:DMEA:Mg^{n}Bu₂ to 2:4:3, resulting in a slightly high yield of 61% based on Mg^{n}Bu₂. Because the NMR signals for the dimethylaminoethanol in complex **2** are relatively broad due to the weak coordination to magnesium, which is discussed in the structure section below, we also attempted to synthesize complex **3** to evaluate the validity of this method. A similar trimetallic structure can be achieved with the 2,6-diisopropylphenol (HL₂) ligand in a stoichiometric ratio of 2:4:3 of HL₂:DMEA:Mg^{n}Bu₂ at 60 °C for 24 h, and the one set of clear
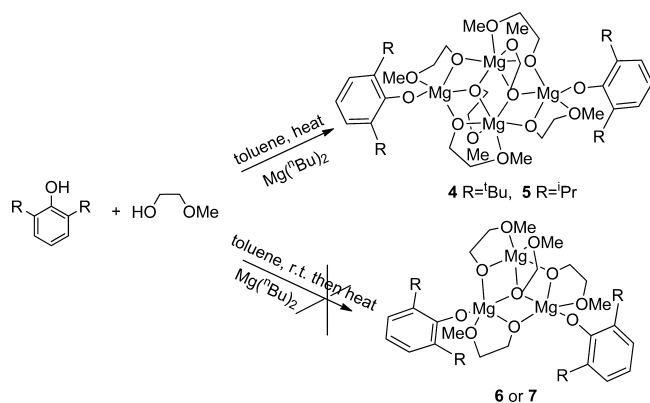
Scheme 1. Synthesis of 1, 2, and 3
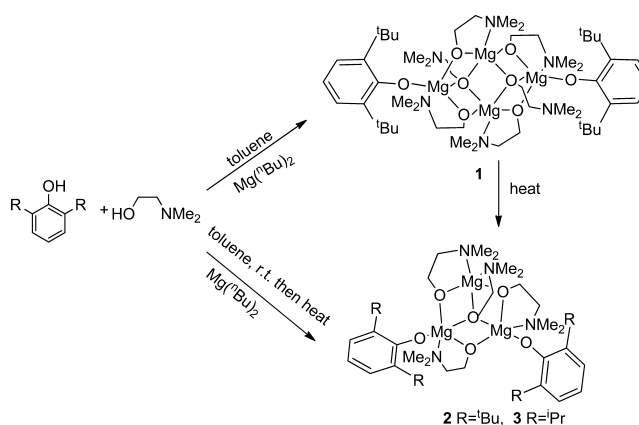
and sharp NMR peaks indicates that thermodynamically stable complex **3** is the main product.

It is interesting that complexes **6** and **7** cannot be obtained by changing the bidentate alcohol to 2-methoxyethanol, even with the exact ratio of 2:4:3. The reaction mixture of 2-methoxyethanol and Mg^{n}Bu₂ with HL₁ or HL₂ afforded complex **4** or **5** in toluene at 60 °C, respectively, which implies that tetrametallic complexes **4** and **5** are more thermodynamically stable, possibly due to the less sterically encumbered alcohol, as deduced from the structure analysis described in Scheme 2.

Complexes **2**, **3**, **4**, and **5** are air-sensitive, colorless crystals and are stable under a nitrogen atmosphere. These complexes are soluble in THF and CH₂Cl₂ and can be purified via recrystallization from THF or CH₂Cl₂/hexane. These complexes were fully characterized by elemental analyses, as well as by ¹H and ¹³C NMR spectroscopy. The results are consistent with their respective formulas.

A single crystal of complex **1** was obtained by cooling a hot THF solution of the reaction mixture and crystallized in monoclinic space group *P*2₁/*n*. An ORTEP drawing of complex **1** is shown in Figure 1. This tetranuclear magnesium

Scheme 2. Synthesis of 4 and 5

trinuclear magnesium clusters in centrosymmetric monoclinic space groups of $P21/c$ and $P21/n$, respectively. The ORTEP drawings for these complexes are depicted in Figures 2 and 3. The two similar trinuclear magnesium clusters have triangular structures in which three Mg atoms are capped by one μ_3 alkoxide above the 3Mg plane. In addition, the other three alkoxides bridge two Mg atoms at each edge. The near right angles of Mg3−O6−Mg1 (93.51(6)°), Mg3−O6−Mg2 (91.46(6)°), and Mg1−O6−Mg2 (98.19(6)°) for **2** and Mg3−O6−Mg1 (95.64(3)°), Mg3−O6−Mg2 (92.23(3)°), and Mg1−O6−Mg2 (96.30(3)°) for **3** suggest that the trinuclear magnesium complexes can be considered cubane-like molecules short of a corner, as shown on the right side of Figures 2 and 3. In these two structures, the three Mg atoms are all pentacoordinated by four O atoms and one N atom for Mg1 and Mg2 and three O atoms and two N atoms for Mg3. In comparison, complex **2** is more crowded because of the t-butyl groups. Therefore, the distances of Mg1−N1 (2.339(2) Å) and Mg2−N3 (2.4542(18) Å) are longer than the related bond distances of Mg1−N1 (2.3172(11) Å) and Mg2−N3 (2.2843(10) Å) in complex **3**, which may imply complex **2** is more active than complex **3** because of the facile substitution of N1 or N3 by LA in the ROP initiating progress. It is notable that the four alkoxy groups can be divided into one inner alkoxide and three peripheral alkoxides. The inner alkoxide bridging three Mg atoms as μ_3 ligand is anticipated to be less active for the ROP of LA than the three μ_2 bridge peripheral alkoxides. In fact, peripheral alkoxides are very active, and the activity of the inner alkoxide is kinetically suppressed in this work.

Single crystals of complexes **4** and **5** were also obtained in THF or CH_2Cl_2/hexane, and they were crystallized as tetranuclear magnesium clusters in centrosymmetric triclinic space group $P\bar{1}$. ORTEP drawings of these complexes are shown in Figures 4 and 5. These two tetranuclear magnesium alkoxide complexes are composed of a rhombus fragment of Mg1−Mg2−Mg1A-Mg2A and the four Mg^{2+} ions lay in the planes defined by the four Mg atoms with almost no deviations. The near right angles of Mg2−O4A−Mg2A (94.89(9)°), Mg2−O4−Mg1 (95.04(9)°), and Mg2A−O4−Mg1
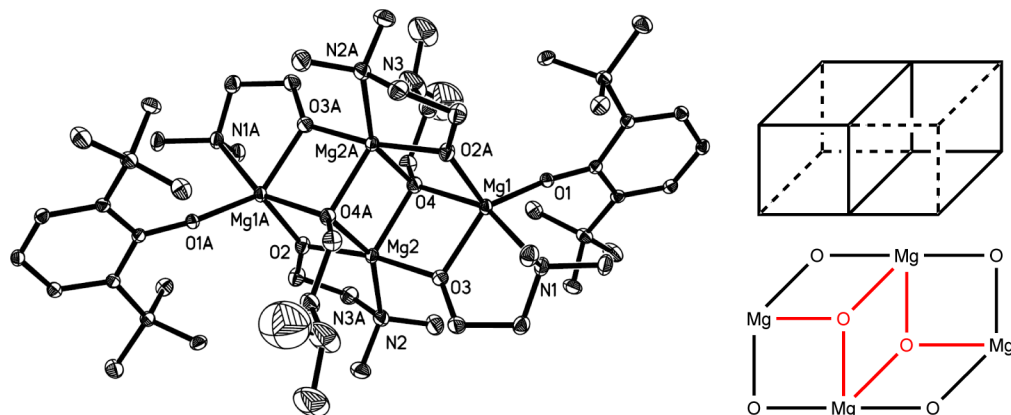
alkoxide complex consists of a rhombus fragment (i.e., Mg1−Mg2−Mg1A−Mg2A), where four edges are supported by μ_2 alkoxides and both triangles are capped by $\mu3$ alkoxides lying on different sides of the rhombus plane. The near right angles of O3−Mg2A−Mg2 (91.53(6)°), Mg2A−O4A−Mg2 (91.13(7)°), Mg2−O4−Mg1 (95.36(7)°), Mg2A−O4−Mg1 (93.91(7)°), O3−Mg2−O4 (82.34(7)°), and O4−Mg2A−O4A (88.87(7)°) suggest that the tetranuclear magnesium complex can also be considered a bis-cubane-like molecule sharing a common plane of Mg2−O4−Mg2A−O4A short of two corners, as shown on the right side of Figure 1. Because the sterically encumbered phenols coordinate to Mg1 and Mg1A, the formation of the rhombic structure is more suitable in terms of energy than the normal cubane-like structure, as shown in Chart 1. In this structure, Mg1 is five-coordinated by O1 of phenol, O2A, O3, O4, and N1 of dimethylaminoethoxy; Mg2 is also pentcoordinated by O2, O3, O4, O4A, and N2 of dimethylaminoethanol. N3 and N3A do not coordinate to Mg, which is most likely due to the sterically crowded dimethylamino group. In addition, the serious vibration of the two noncoordinated dimethylamino groups may give rise to the thermodynamic instability of complex **1**.

Single crystals of complexes **2** and **3** were prepared in a solution of THF, and these complexes were crystallized as

Figure 1. ORTEP drawing of complex **1** with thermal ellipsoids at the 30% probability level. Selected bond lengths: Mg1−O1, 1.9270(17) Å; Mg1−O2, 1.9971(19) Å; Mg1−O3, 2.0054(19) Å; Mg1−O4, 2.1755(18) Å; Mg1−N1, 2.347(2) Å; Mg2−O3, 1.961(2) Å; Mg2−O2, 1.9974(19) Å; Mg2−O4, 2.040(2) Å; Mg2−O4A, 2.074(2) Å; Mg2−N2, 2.209(2) Å; Mg1−Mg2A, 3.1063(10) Å; Mg1−Mg2, 3.1173(10) Å; Mg2−Mg2A, 2.9379(16) Å; and Mg2−Mg1A, 3.1063(10) Å. Selected bond angles: O3−Mg1−O4, 78.02(7)°; O3−Mg2−O2, 171.75(9)°; O3−Mg2−O4, 82.34(7)°; O4−Mg2A−O4A, 88.87(7)°; O3−Mg2−N2, 94.18(8)°; O2−Mg2−N2, 80.91(8)°; O4−Mg2−N2, 117.02(8)°; O4A−Mg2−N2, 152.12(8)°; O3−Mg2A−Mg2, 91.53(6)°; Mg2A−O4A−Mg2, 91.13(7)°; Mg2−O4−Mg1, 95.36(7)°; and Mg2A−O4−Mg1, 93.91(7)°. Symmetry code: −x, 1 − y, 1 − z.
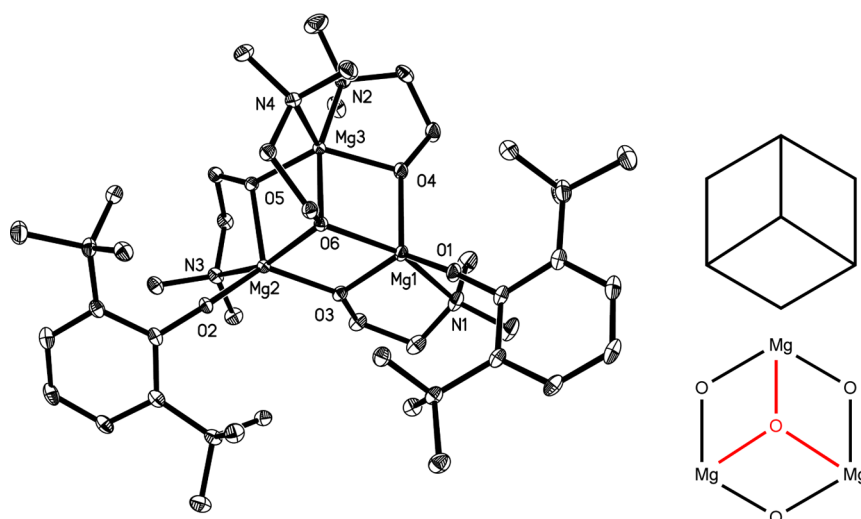
Figure 2. ORTEP drawing of complex **2** with thermal ellipsoids at the 30% probability level. Selected bond lengths: Mg1−Mg3, 3.0409(9) Å; Mg1−Mg2, 3.1863(9) Å; Mg2−Mg3, 2.9924(9) Å; Mg1−O1, 1.9170(15) Å; Mg1−O4, 1.9935(16) Å; Mg1−O3, 2.0150(15) Å; Mg1−O6, 2.1057(15) Å; Mg1−N1, 2.339(2) Å; Mg2−O2, 1.9303(15) Å; Mg2−O3, 1.9683(15) Å; Mg2−O5, 2.0148(15) Å; Mg2−O6, 2.1103(15) Å; Mg2−N3, 2.4542(18) Å; Mg3−O5, 1.9397(15) Å; Mg3−O4, 1.9744(15) Å; Mg3−O6, 2.0686(15) Å; Mg3−N4, 2.178(2) Å; Mg3−N2, 2.235(2) Å. Selected bond angles: Mg3−O6−Mg1, 93.51(6)°; Mg3−O6−Mg2, 91.46(6)°; Mg1−O6−Mg2, 98.19(6)°; Mg2− O3−Mg1, 106.24(7)°; Mg3−O4−Mg1, 100.06(7)°; Mg3−O5−Mg2, 98.33(6)°; O4−Mg1−O3, 105.92(6)°; O4−Mg1−O6, 80.94(6)°; O3−Mg1−O6, 77.21(6)°; O2−Mg2−O3, 128.68(7)°; O3−Mg2−O5, 110.88(6)°; O3−Mg2−O6, 78.10(6)°; O5−Mg3−O6, 84.01(6)°; O5−Mg3−O4, 126.38(7)°; and O5−Mg3−O6, 84.01(6)°.
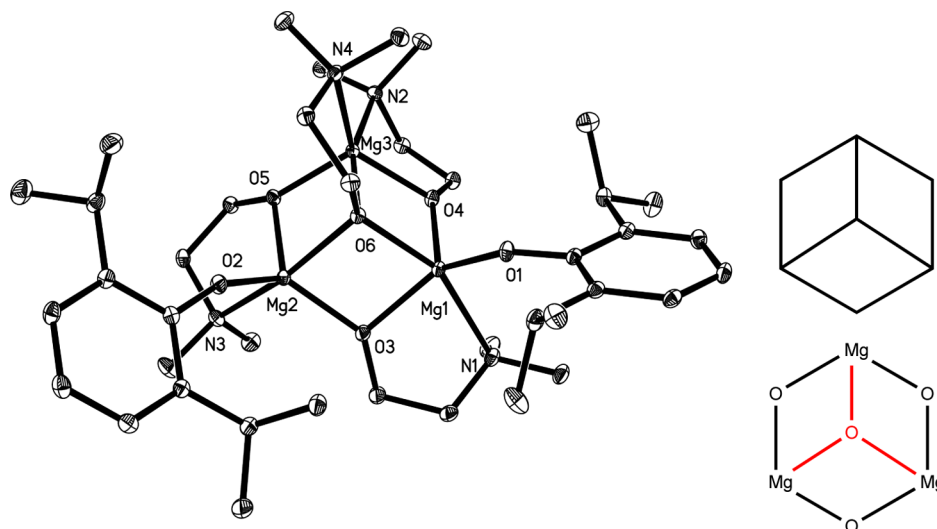

Figure 3. ORTEP drawing of complex **3** with thermal ellipsoids at the 30% probability level. Selected bond lengths: Mg1−Mg3, 3.0404(5) Å; Mg2−Mg3, 2.9842(5) Å; Mg2−Mg1, 3.0915(5) Å; Mg2−O2, 1.8938(9) Å; Mg2−O3, 1.9589(9) Å; Mg2−O5, 2.0255(9) Å; Mg2−O6, 2.0937(9) Å; Mg2−N3, 2.2843(10) Å; Mg1−O1, 1.9198(9) Å; Mg1−O4, 1.9867(9) Å; Mg1−O3, 2.0224(9) Å; Mg1−O6, 2.0564(9) Å; Mg1−N1, 2.3172(11) Å; Mg3−O5, 1.9364(9) Å; Mg3−O4, 1.9778(9) Å; Mg3−O6, 2.0464(9) Å; Mg3−N4, 2.1916(10) Å; Mg3−N2, 2.2178(11) Å. Selected bond angles: Mg3−O5−Mg2, 97.72(4)°; Mg3 −O4−Mg1, 100.15(4)°; Mg3−O6−Mg1, 95.64(3)°; Mg3−O6−Mg2, 92.23(3)°; and Mg1−O6−Mg2, 96.30(3)°.

(94.60(9)°) for **4** and Mg2A−O4−Mg2 (96.77(6)°), Mg2A−O4−Mg1 (95.09(7)°), and Mg2−O4−Mg1 (93.77(6)°) for **5**, suggest that the tetranuclear magnesium complex can also be considered a bis-cubane-like molecule sharing a common plane of Mg2−O4−Mg2A−O4A short of two corners, as shown in the right side of Figures 4 and 5. Six-coordinated Mg2 and Mg2A in complexes **4** and **5** are different from the related Mg atoms, which are just pentacoordinated in complex **1**, clearly because of the more crowded dimethylamino group, compared to the methoxy group. The Mg atoms tend to be octahedrally coordinated when permitted by the surrounding environment. Therefore, we believe that tetranuclear complexes **4** and **5** are more thermodynamically stable than the unsynthesized

complexes **6** and **7**. Because the sterically encumbered phenols coordinate to Mg1 and Mg1A, the formation of the rhombic structure is more suitable in terms of energy than the normal cubic-like structure, as shown in Chart 1. It is also worth to note that the six alkoxy groups in the two complexes can be divided into two inner alkoxides and four peripheral alkoxides. The inner alkoxides bridging three Mg atoms as μ_3 ligand are anticipated to be less active for the ROP of lactide than the four μ_2 bridge peripheral alkoxides. In fact, our experimental results indicate that the peripheral alkoxides are also very active, and the activities of the inner alkoxides are kinetically suppressed, as observed for complexes **2** and **3**.
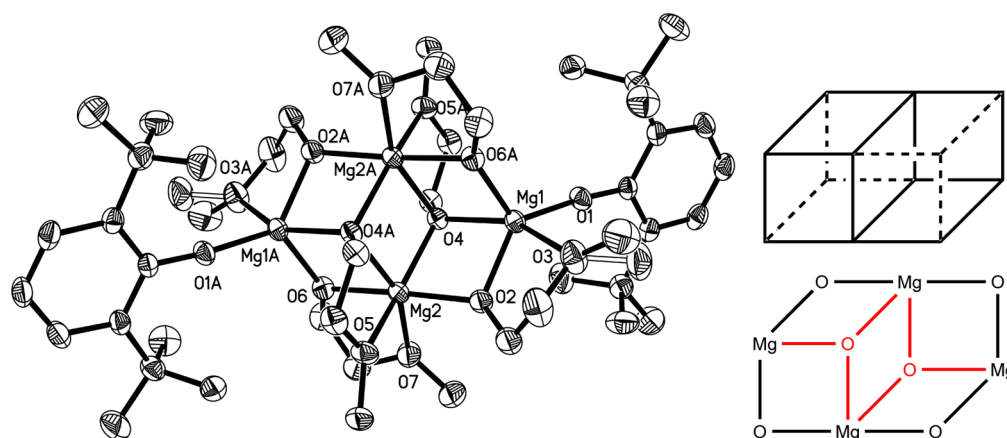
Figure 4. ORTEP drawing of complex **4** with thermal ellipsoids at the 30% probability level. Selected bond lengths: Mg2−Mg2A, 3.090(2) Å; Mg2−Mg1A, 3.1100(15) Å; Mg2−Mg1, 3.1108(15) Å; Mg1−O1, 1.893(2) Å; Mg1−O6A, 1.946(3) Å; Mg1−O2, 1.976(3) Å; Mg1−O4, 2.127(2) Å; Mg1−O3, 2.344(3) Å; Mg1−Mg2, 3.1099(15) Å; Mg2−O2, 1.997(3) Å; Mg2−O6, 2.025(3) Å; Mg2−O4, 2.090(2) Å; Mg2−O4, A2.105(2) Å; Mg2−O7, 2.134(3) Å; and Mg2−O5, 2.201(2) Å. Selected bond angles: Mg2−O4A−Mg2A, 94.89(9)°; Mg2−O4−Mg1, 95.04(9)°; Mg2A−O4−Mg1, 94.60(9)°; O2−Mg2−O4, 79.45(10)°; O4−Mg2A−O4A, 85.11(9)°; O2−Mg2−O6, 172.10(11)°; O2−Mg1−O4, 79.03(10)°; and O6A−Mg1−O4, 81.58(10)°. Symmetry code = 2 − x, −y, −z.
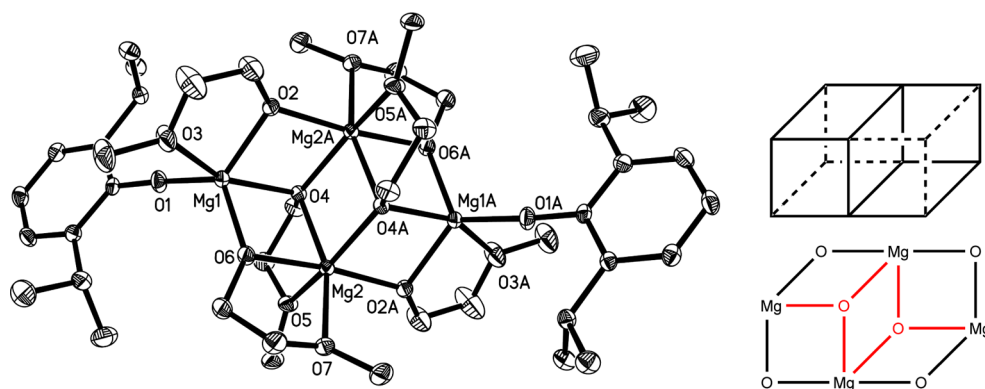

Figure 5. ORTEP drawing of complex **5** with thermal ellipsoids at the 30% probability level. Selected bond lengths: Mg1−Mg2, 3.0650(13) Å; Mg1−Mg2A, 3.0803(12) Å; Mg2−Mg1A, 3.0803(12) Å; Mg2−Mg2A, 3.1052(14) Å; Mg1−O1, 1.8769(19) Å; Mg1−O6, 1.9508(17) Å; Mg1−O2, 1.9795(17) Å; Mg1−O4, 2.1101(17) Å; Mg1−O3, 2.177(2) Å; Mg2−O2A, 1.9808(17) Å; Mg2−O6, 2.0170(18) Å; Mg2−O4A, 2.0648(16) Å; Mg2−O4, 2.0886(16) Å; Mg2−O7, 2.1462(17) Å; Mg2−O5, 2.1711(17) Å. Selected bond angles: Mg2A−O4−Mg2, 96.77(6)°; Mg2A−O4−Mg1, 95.09(7)°; Mg2−O4−Mg1, 93.77(6)°; O2A−Mg2−O6, 171.44(8)°; O2A−Mg2A−O4, 80.09(7)°; O6−Mg2A−O4, 100.24(7)°; O6−Mg2−O4, 81.71(7)°; and O4A−Mg2−O4, 83.23(6)°. Symmetry code = 1 − x, 1 − y, −z.

Ring-Opening Polymerization of ʟ-Lactide Initiated by Clusters 2 and 3.
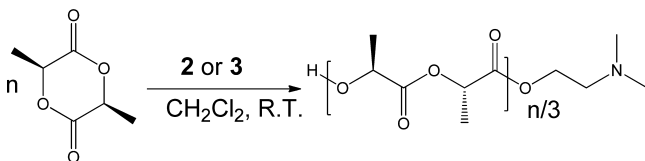
The ring-opening polymerizations (ROP) of ʟ-lactide (ʟ-LA) employing magnesium alkoxide clusters **2** and **3** as initiators were systematically examined. Representative results are collected in Table 1. The polymerizations of ʟ-lactide almost went to completion in 5 and 20 min for **2** and **3**, respectively, when a 400:1 (monomer: initiator) ratio was used (entries 4 and 12 in Table 1) with a complex concentration of 1 mM in CH_2Cl_2 (10 mL) at 30 °C. Therefore, complex **2** is more active than **3**, which is most likely due to the more crowded t-butyl groups, resulting in weak coordination between the dimethylamino groups and the Mg atom and the lactide monomer easily coordinating to magnesium in the initiating stage. The repulsion of the bulky t-butyl groups may also lead to a highly active Mg-alkoxide bond in the lactide insertion reaction during the propagation process. The number-average molecular weights (Mn determined from GPC) of the produced polymers are similar to the calculated molecular weights based on three polymer chains growing per one molecular cluster in which the less-active inner alkoxide is possibly kinetically suppressed by the three preferred active peripheral alkoxides. The ROP initiated by cluster **2** are living,[15] which can be elucidated by the fact that the molecular weights of the polymers increased linearly with the ratio of $[LA]_0:[2]_0$ ranging from 100:1 to 500:1 (see entries 1−5 in Table 1, and Figure 6) and the narrow PDIs (1.02−1.16). The performance of the living polymerization was further confirmed by second feed experiments (entry 10) in which another portion of the ʟ-LA monomer was added after the polymerization of the first addition of ʟ-LA was completed. Moreover, complex **2** can polymerize up to 4000 equiv of ʟ-LA at ambient temperature within 1 min with a controlled molecular weight and narrow PDI. Comparing to the highly active dimeric magnesium alkoxides supported by complicated bulky ligands reported

Table 1. Ring-Opening Polymerization (ROP) of L-Lactide (L-LA) Initiated by Magnesium Clusters 2 and 3[a]

entry	complex	$[LA]_0/[I]_0$	t (min)	conversion (%)[b]	M_{cal} (g mol^{-1})[c]	M_{obs} (g mol^{-1})[d]	polydispersity index, PDI
1	2	100:1	5	92	4500	5600	1.16
2	2	200:1	5	>99	9600	10500	1.13
3	2	300:1	5	97	14000	15600	1.10
4	2	400:1	5	98	19000	20000	1.16
5	2	500:1	5	98	24000	23000	1.12
6	2	1000:1	1	90	44000	55000	1.16
7	2	2000:1	1	95	91000	81000	1.07
8	2	3000:1	1	87	125000	94100	1.03
9	2	4000:1	1	71	136000	102100	1.02
10[e]	2	200(200):1	5(5)	>99	20000	23000	1.17
11[f]	2	600:1	1	>99	29000	30000	1.19
12	3	400:1	20	89	19000	17000	1.08
13[g]	2	100:1	8	>99	4900	5100	1.30
14[g]	2	200:1	8	87	8440	10400	1.63
15[g]	2	300:1	8	87	13000	14000	1.56
16[g]	2	400:1	8	80	15500	16000	1.52
17[g]	2	500:1	8	70	17000	16400	1.43
18[g]	2	1000:1	8	72	35000	37000	1.44

[a]Reactions performed in 10 mL of dichloromethane at 30 °C, $[Cat.]_0$ = 1.0 mM. [b]Lactide conversion as determined by ^{1}H NMR. [c]Calculated from the molecular weight of L-LA times $[LA]_0/3$ times monomer conversion plus M_{DMEA}. [d]Obtained from GPC analysis and calibrated using a polystyrene standard and corrected using the Mark−Houwink factor of 0.58. [e]Polymerization of L-LA with complex 2 for 5 min followed by the addition of another portion of L-LA. [f]Reactions performed in 10 mL of toluene at 30 °C, $[Cat.]_0$ = 0.17 mM. [g]Melt polymerization at 110 °C.
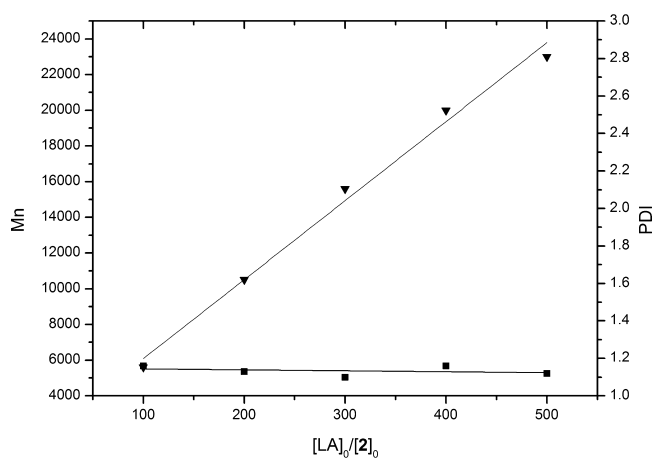

Figure 6. Relationship between Mn (▼)/PDI (■) of the polymer and the initial molar ratios $[LA]_0/[2]_0$ for polymerization of L-LA initiated by complex 2 in dichloromethane at room temperature (see entries 1−5 in Table 1).

Figure 7. ^{1}H NMR analysis of poly(L-LA) obtained from polymerization of L-LA initiated by complex 2.

previously by us and the Lin group,[6b,k] complex 2 can show slightly higher activity for ROP of LA in CH_2Cl_2 at room temperature, even with a low concentration of $[Mg]_0$. The ^{1}H NMR of the PLA-50:1 produced from complex 2 at an initial $[LA]_0/[complex]_0$ ratio of 50:1 exhibits a characteristic quadruple methine peak (Figure 7) at 5.16 ppm, indicating no serious epimerization of the chiral centers in the polymers, which was also confirmed using homonuclear-decoupled ^{1}H NMR studies in the methine region. The peaks at 4.23 ppm ($-CH_2OCH_2N(CH_3)_2$), 2.56 ppm ($-CH_2N(CH_3)_2$), and 2.26 ppm ($-N(CH_3)_2$) correspond to the dimethylamino group $[OCH_2CH_2N(CH_3)_2]$, and the peak at 4.34 ppm was assigned to the methine hydrogen in the polymer terminal group of (HOCHMe−). The integral ratio of the dimethylamino group to the methine hydrogen indicates that the polymer chain is capped with one dimethylamino group and one hydroxyl group, which suggests that the polymerization occurs via insertion of L-
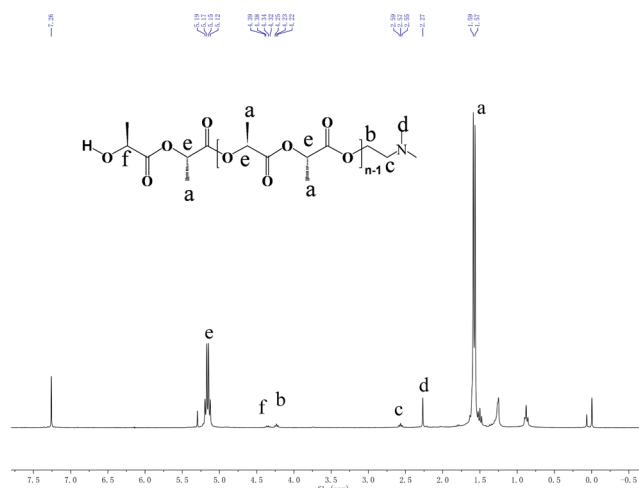
LA into the magnesium-alkoxy bond. The ESI mass spectrum of the final polymer, shown in Figure 8, also confirmed the coordination insertion mechanism evidenced by the series of peaks at $72m+89+1$, which can be assigned to $(CH_3)_2NCH_2OH + m(C_3H_4O_2) + H^+$.[16] Complex 2 was also employed to initiate the melt polymerization of L-lactide at 110 °C with various $[LA]_0/[complex]_0$ ratios ranging from 100:1 to 1000:1 (see entries 13−18 in Table 1), and the molecule weights are close to the expected values. The PDIs of the final polymers (1.3−1.63) are slightly broad, which can be attributed to the low diffusion of the monomer in the highly viscous melt polymerization system as well as to some side reactions at high temperature.
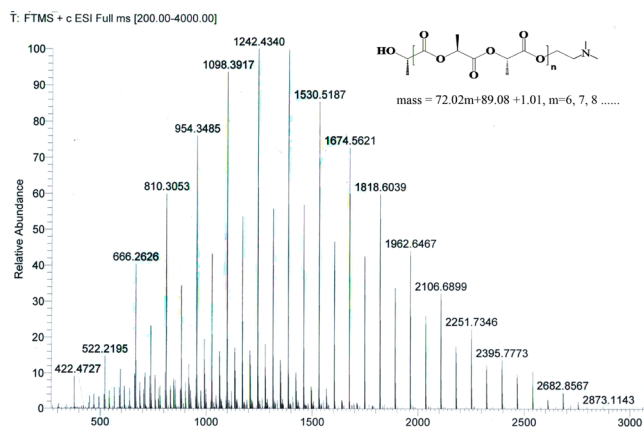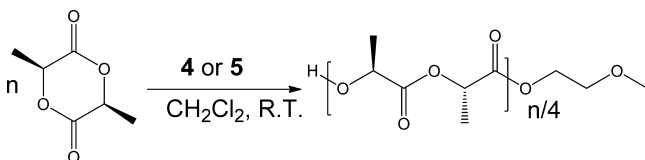
Figure 8. ESI-MS spectrum of poly(L-LA) prepared by ROP of L-LA.

Figure 9. Relationship between Mn (▼)/PDI (■) of the polymer and the initial molar ratios $[LA]_0/[4]_0$ for the polymerization of L-LA initiated by complex **4** in dichloromethane at room temperature (see entries 1−5 in Table 2).

Ring-Opening Polymerization of L-Lactide Initiated by Clusters 4 and 5.

Ring-opening polymerizations (ROP) of L-LA employing magnesium clusters **4** and **5** as initiators were also conducted. Representative results are provided in Table 2. The polymerization was nearly complete in 6 min for **4** with an initiator/monomer ratio of 1:150 and in 60 min for complex **5** with a conversion of 70%. Therefore, complex **4** is more active than complex **5**, which is similar to the results obtained for complexes **2** and **3** possibly for similar reasons, and the activity of complex **4** is similar to that of complex **2** (see entries 1 and 9 in Table 2). The number-average molecular weights of the produced polymers are also close to the calculated molecular weights based on four polymer chains growing per one molecular cluster, in which the two less active inner alkoxides are kinetically suppressed by the four very active peripheral alkoxides. The polymerization progress is living, as shown in Figure 9, and the polymers were obtained with desirable molecular weights and narrow PDIs (see entries 1−6 in Table
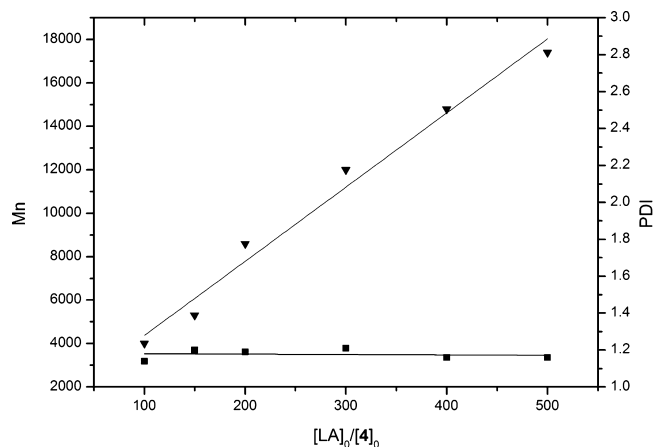
2). The final polymer with a ratio of 50:1 (monomer: complex **4**) shows peaks at 4.29 ppm (OCH_2−), 3.58 ppm (−CH_2−OCH$_3$), 3.37 ppm (−OCH_3), and 4.34 ppm (HOCHMe−) indicating the presence of terminal groups of methoxyethanoxy and hydroxyl groups, which confirms that the polymerization proceeds via insertion of L-lactide into the magnesium-alkoxy bond (Figure 10).[17] The end groups of this obtained oligomer were analyzed and approved by ESI-MASS too (Figure 11). The high activity of complex **4** was also verified by ROP of 2000 equiv, which was completed in 3 min and produced a molecular weight and narrow PDI that were close to the expected values (entry 8 in Table 2). Melt polymerizations of L-lactide using complex **4** as the initiator at various $[LA]_0/$[complex]$_0$ ratios ranging from 200:1 to 500:1 (see entries 10−13 in Table 2) are performedunder controlled model yielding the expected molecule weights with slightly broad PDIs for the final polymers (1.38−1.40), which might be due to the low rate of diffusion of lactide in the highly viscous melt polymerization system.

Ring-Opening Polymerization of *rac*-Lactide. Polymerizations of *rac*-lactide by complexes **2**−**5** were also performed, and the results are shown in Table 3. The homonuclear

Table 2. ROP of L-Lactide Initiated by Magnesium Clusters 4 and 5[a]

entry	complex	$[LA]_0/[I]_0$	t (min)	conversion (%)[b]	M_{cal} (g/mol)[c]	M_{obs} (g/mol)[d]	polydispersity index, PDI
1	4	100:1	6	97	3500	4000	1.14
2	4	150:1	6	95	5200	5300	1.20
3	4	200:1	6	>99	7300	8600	1.19
4	4	300:1	6	95	11000	12000	1.21
5	4	400:1	6	94	14000	14800	1.16
6	4	500:1	6	91	16400	17400	1.16
7	4	1000:1	4	82	29500	29600	1.14
8	4	2000:1	3	70	50000	41000	1.04
9	5	150:1	60	70	3800	3500	1.06
10[e]	4	200:1	8	96	7000	8700	1.38
11[e]	4	300:1	8	91	10000	11000	1.40
12[e]	4	400:1	8	83	12000	11000	1.40
13[e]	4	500:1	8	80	14500	13000	1.38

[a]Reactions performed in 10 mL of dichloromethane at 30 °C, [Cat.] = 1.0 mM. [b]Lactide conversion as determined by ^{1}H NMR. [c]Calculated from the molecular weight of L-LA times $[LA]/3$ times monomer conversion yield plus $M_{methoxyethanol}$. [d]Obtained from GPC analysis, calibrated using polystyrene standard and corrected using the Mark−Houwink factor of 0.58. [e]Melt polymerization at 110 °C.
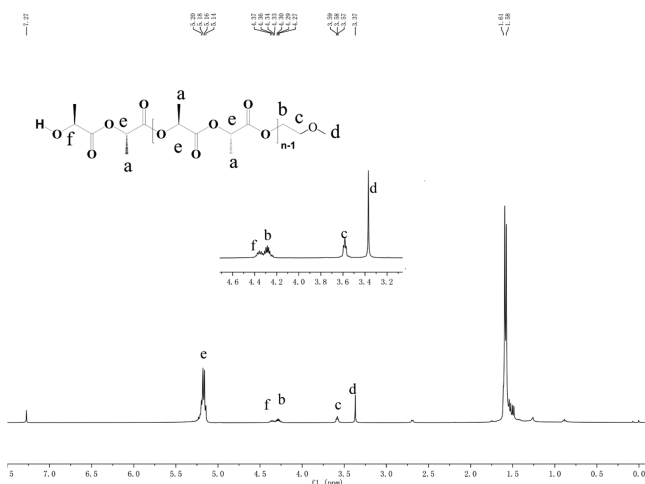
Figure 10. ^{1}H NMR analysis of poly(L-LA) obtained from polymerization of L-LA initiated by complex **4** with a $[LA]_0:[4]_0$ ratio of 50:1.
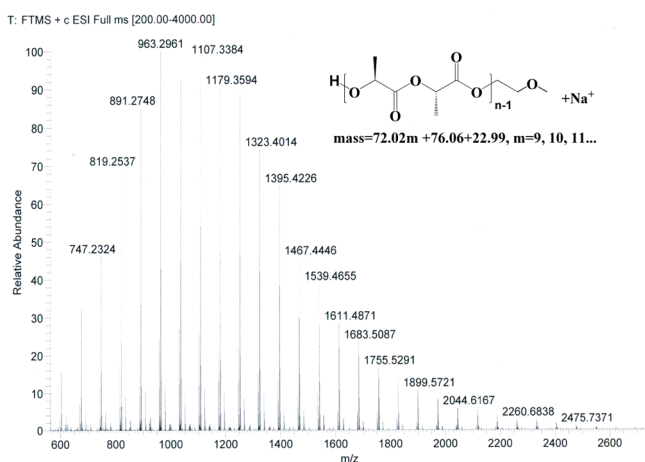

Figure 11. ESI-MS spectrum of poly(L-LA) prepared by ROP of L-LA with a $[LA]_0:[4]_0$ ratio of 50:1.

decoupled ^{1}H NMR spectra in the methine region of the PLA derived from complexes **2−5** reveal that only slightly heterotactic polymers were obtained with Pr = 0.55, 0.54, 0.61, 0.56 for complexes **2−5**, respectively, when CH$_2$Cl$_2$ was used as the solvent.[18] No improvements can be achieved by alternating the solvent to toluene or THF. The low selectivity may result from the insufficient bulk of the ligand. The modification of this type of ligand is now in progress in our laboratory.

Kinetics Studies Using 3 and 5 as Initiators. Kinetics studies were conducted to gain insight into the polymerization progress for these trinuclear and tetranuclear magnesium

alkoxide clusters. For experimental ease, the less active complexes (i.e., **3** and **5**) were employed in the kinetics studies. The polymerization rates were analyzed in CH$_2$Cl$_2$ at 30 °C and monitored by ^{1}H NMR using a fixed monomer concentration ($[LA]_0 = 0.2$ M) and various concentrations of complex **3** (0.9−1.1 mM). The plots of $\ln([LA]_0/[LA]_t)$, as a function of time, exhibited a good linear relationship. This linear relationship indicates that the polymerization proceeds with a first-order dependence on the monomer concentration (see Figure S1 in the Supporting Information, $k_{obs} = 0.087$ min^{-1}, $[LA]_0 = 0.2$ M, $[3]_0 = 0.9$ mM). The experimental gradient of the least-squares fitted line for $\ln(k_{obs})$ vs $\ln[3]_0$ was 0.97(5), which is consistent with a first-order dependence on $[3]_0$ (Figure S2 in the Supporting Information). Therefore, the overall rate equation is

$$-\frac{d[LA]}{dt} = k[LA]^1[3]^1 \quad (k = 94.42 \text{ M}^{-1} \text{ min}^{-1})$$

The kinetics initiated by tetranuclear complex **5** was also studied in CH$_2$Cl$_2$ at 30 °C ($[LA]_0 = 0.2$ M, $[5]_0 = 1.5−2.75$ mM). In this system, plots of $(1/[LA]_t - 1/[LA]_0)$ versus time are linear, indicating that the polymerization proceeds with a second-order dependence on the monomer concentration (Figure S3 in the Supporting Information, $k_{obs} = 0.2145$ M^{-1} min^{-1}, $[LA]_0 = 0.2$ M, $[5]_0 = 1.5$ mM). The experimental gradient of the least-squares fitted line for $\ln(k_{obs})$ vs $\ln[5]_0$ was 0.95(1), implying that the polymerization proceeds with a first-order dependence on $[5]_0$ (Figure S4 in the Supporting Information). The rate law of

$$-\frac{d[LA]}{dt} = k[LA]^2[5]^1 \quad (k = 137.08 \text{ M}^{-2} \text{ min}^{-1})$$

is the same as that determined in our previous dinuclear magnesium system.[5j]

The results of the polymerization kinetics studies indicate a first-order dependence on both $[LA]$ and $[3]$ when complex **3** is used as the initiator. When complex **5** is used as the initiator, the polymerization rate has a second-order dependence on $[LA]$ and a first-order dependence on $[5]$. These results are reasonable because trinuclear complex **3** is too crowded to simultaneously activate two lactides. However, the simultaneous activation of two lactides is possible for the less bulky tetranuclear complex **5**. The second-order dependence on $[LA]$ for complex **5** can also be attributed to the symmetry of tetranuclear complex **5** where the four Mg atoms can be divided into two identical parts with a long distance separation related by an inversion center. Therefore, it is possible that the two lactides can be activated at the two parts at the same time.

Based on the NMR and mass spectra of the final polymers, the ROP polymerization mechanism for this system is a coordination−insertion mechanism. As Duda and Penczek et al.

Table 3. ROP of *rac*-Lactide Initiated by Magnesium Clusters 2, 3, 4, and 5[a]

entry	complex	$[rac\text{-}LA]_0/[I]_0$	t (min)	conversion (%)[b]	M_{cal} (g/mol)[c]	M_{obs} (g/mol[d])	polydispersity index, PDI	Pr
1	**2**	200	6	95	9200	8900	1.20	0.55
2	**3**	200	30	57	5600	5000	1.07	0.54
3	**4**	200	7	96	7000	8700	1.33	0.61
4	**5**	200	70	51	3800	2800	1.01	0.56

[a]Reactions performed in 10 mL of dichloromethane at 30 °C, $[Cat.]_0 = 1.0$ mM. [b]Lactide conversion as determined by ^{1}H NMR. [c]Calculated from the molecular weight of *rac*-LA times $[LA]_0/3$ times monomer conversion plus M_{DMEA} or *rac*-LA times $[LA]_0/4$ times monomer conversion yield plus $M_{methoxyethanol}$. [d]Obtained from GPC analysis, calibrated by polystyrene standard and corrected using the Mark−Houwink factor of 0.58.

pointed out, the alkoxides in aggregated and nonaggregated Sn(OBu)$_2$[7e] can show different activities toward ROP of LA; it is reasonable, to a certain extent, to propose that peripheral alkoxides are more active than inner alkoxide for ROP of LA in highly active alkoxide clusters **2−5**, because of different environmental factors. But the actual intermediates in the polymerization progress still cannot be determined, because of the absence of direct evidence, which will be the subject of further, future investigations.

■ CONCLUSION

Five magnesium alkoxide clusters supported by two bulky phenols were synthesized, in which the triangular structures are thermodynamically stable for magnesium alkoxide clusters with 2-N,N-dimethylaminoethanol as the alcohol, and the rhombic structures are thermodynamically stable for magnesium alkoxide clusters with methoxyethanol as the alcohol. The ring-opening polymerization (ROP) results show that the four thermodynamically stable complexes are highly active yielding desirable molecular weights with narrow PDIs. In addition, complex **2** was able to initiate the polymerization of 4000 equiv of lactide (LA) in 1 min. Because of the different steric environments in the trinuclear magnesium and tetranuclear magnesium clusters, the kinetics studies indicated that the polymerization was first-order in both the trinuclear magnesium complex **3** and LA. However, for tetranuclear magnesium complex **5**, the polymerization rate was first-order in **5** and second order in LA.

■ EXPERIMENTAL SECTION

All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry nitrogen atmosphere, using standard Schlenk techniques or a glovebox. Hexane, toluene, and tetrahydrofuran (THF) were distilled over sodium benzophenone. CH$_2$Cl$_2$ was distilled from P$_2$O$_5$. 2-N,N-Dimethylaminoethanol and methoxyethanol were dried with CaH$_2$ for 24 h at 60 °C and then distilled under a nitrogen atmosphere. L-LA was purchased from Daigang BIO Engineer Limited Co. of China and recrystallized from toluene. Mg^{n}Bu$_2$ (1 mol/L in hexane) and various phenols were purchased from Acros Company. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 600 MHz or a 300 MHz spectrometer. ^{1}H NMR chemical shifts are reported in ppm versus the residual protons in deuterated solvents as follows: δ 7.26 CDCl$_3$, ^{13}C NMR chemical shifts are reported in ppm versus residual ^{13}C in the solvent: δ 77.0. The mass spectroscopic data were obtained using a Thermo Scientific Orbitrap Elite MS (LTQ Orbitrap Elit).

Synthesis of Complex 1. A mixture of Mg^{n}Bu$_2$ (5.1 mL, 5.1 mmol), DMEA (0.5 mL, 5.0 mmol), and 2,6-di-*tert*-butylphenol (1.15 g, 5 mmol) in toluene was stirred at 0 °C for 1 h. The solution was stirred at room temperature for 24 h. A pale yellow haze gradually formed. The solvent then was removed under vacuum, and recrystallization with hexane afforded a solid white mixture.

Synthesis of Complex 2. A mixture of Mg^{n}Bu$_2$ (3.8 mL, 3.8 mmol), DMEA (0.5 mL, 5.0 mmol), and 2,6-di-*tert*-butylphenol (0.575 g, 2.5 mmol) in toluene was stirred at 0 °C for 1 h. Next, the solution was heated to 60 °C and stirred for 24 h. A dark yellow haze gradually formed. Then, the solvent was removed under vacuum, and recrystallization with hexane afforded white solid. Yield: 0.61 g (61%). Anal. Calcd for

C$_{44}$H$_{82}$Mg$_3$N$_4$O$_6$: C 63.21, H 9.89, N 6.70. Found: C 63.25, H 9.80, N 6.74. ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 7.18 (s, Ar−H, 4H), 6.42 (m, Ar−H, 2H), 4.08−3.81 (m, −CH$_2$O, 8H), 2.68 (s, N(CH$_3$)$_2$, 3H), 2.59 (s, N(CH$_3$)$_2$, 6H), 2.47−2.33 (m, N(CH$_3$)$_2$, 15H), 2.24−2.07 (m, −CH$_2$N(CH$_3$)$_2$, 8H), 1.60 (s, C(CH$_3$)$_3$, 36H); ^{13}C NMR (150 MHz, CDCl$_3$): δ (ppm) 167.32 (Ar), 165.27 (Ar), 137.43 (Ar), 136.86 (Ar), 128.88 (Ar), 128.07 (Ar), 125.15 (Ar), 124.76 (Ar), 124.20 (Ar), 137.43 (Ar), 123.71 (Ar), 109.98 (Ar), 65.38 (−CH$_2$OCH$_2$N-(CH$_3$)$_2$), 64.84 (−CH$_2$OCH$_2$N(CH$_3$)$_2$), 63.63 (−CH$_2$OCH$_2$N(CH$_3$)$_2$), 58.66 (−CH$_2$N(CH$_3$)$_2$), 58.08 (−CH$_2$N(CH$_3$)$_2$), 57.19 (−CH$_2$N(CH$_3$)$_2$), 47.11 (N(CH$_3$)$_2$), 46.49 (N(CH$_3$)$_2$), 45.80 (N(CH$_3$)$_2$), 43.69 (N(CH$_3$)$_2$), 35.07 (−C(CH$_3$)$_3$), 30.52 ((CH$_3$)$_3$), 30.11 ((CH$_3$)$_3$).

Synthesis of Complex 3. A mixture of Mg^{n}Bu$_2$ (3.8 mL, 3.8 mmol), DMEA (0.5 mL, 5.0 mmol), and 2,6-diisopropyl-phenol (0.445 g, 2.5 mmol) in toluene was stirred at 0 °C for 1 h. Next, the solution was heated to 60 °C and stirred for 24 h. A white haze gradually formed. The solvent then was removed under vacuum, and recrystallization with hexane afforded a white solid. Yield: 0.39 g (40%). Anal. Calcd. for C$_{40}$H$_{74}$Mg$_3$N$_4$O$_6$: C 61.60, H 9.56, N 7.18. Found: C 62.0, H 9.62, N 7.06. ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 6.98 (d, Ar−H, 2H, J = 7.2 Hz), 6.93 (d, Ar−H, 2H, J = 7.2 Hz), 6.46 (dd, Ar−H, 1H, J = 7.2 Hz), 6.42 (dd, Ar−H, 1H, J = 7.2 Hz), 3.96−3.85 (m, −CH$_2$O, 8H), 3.59−3.52 (m, −CH$_2$N, 6H), 3.21−3.17 (m, −CH(CH$_3$)$_2$, 1H), 3.07−3.02 (m, −CH(CH$_3$)$_2$, 1H), 2.73−2.69 (m, −CH(CH$_3$)$_2$, 2H), 2.54−2.52 (m, N(CH$_3$)$_2$, 6H), 2.46 (s, N(CH$_3$)$_2$, 3H), 2.36−2.24 (m, N(CH$_3$)$_2$, 15H), 2.06 (t, −CH$_2$N, 2H), 1.27−1.56 (m, −CH(CH$_3$)$_2$, 24H); ^{13}C NMR (150 MHz, CDCl$_3$): δ (ppm) 160.92 (Ar), 160.79 (Ar), 135.68 (Ar), 122.13 (Ar), 110.86 (Ar), 110.67 (Ar), 64.85 (−CH$_2$OCH$_2$N(CH$_3$)$_2$), 64.29 (−CH$_2$OCH$_2$N(CH$_3$)$_2$), 64.01 (−CH$_2$OCH$_2$N(CH$_3$)$_2$), 62.61 (−CH$_2$OCH$_2$N(CH$_3$)$_2$), 59.04 (−CH$_2$N(CH$_3$)$_2$), 58.44 (−CH$_2$N(CH$_3$)$_2$), 58.00 (−CH$_2$N(CH$_3$)$_2$), 56.79 (−CH$_2$N-(CH$_3$)$_2$), 47.00 (N(CH$_3$)$_2$), 46.31 (N(CH$_3$)$_2$), 46.16(N-(CH$_3$)$_2$), 45.68 (N(CH$_3$)$_2$), 45.22 (N(CH$_3$)$_2$), 4.52 (N(CH$_3$)$_2$), 43.69 (N(CH$_3$)$_2$), 42.96 (N(CH$_3$)$_2$), 27.02 (−CH(CH$_3$)$_2$), 25.54 (−CH(CH$_3$)$_2$), 24.35 (−(CH$_3$)$_2$), 23.76 (−(CH$_3$)$_2$), 22.69 (−(CH$_3$)$_2$).

Synthesis of Complex 4. A mixture of Mg^{n}Bu$_2$ (5.1 mL, 5.1 mmol), 2-methoxyethanol (0.6 mL, 7.5 mmol), and 2, 6-di-*tert*-butylphenol (0.575 g, 2.5 mmol) in toluene was stirred at 0 °C for 1 h. Next, the solution was heated to 60 °C and stirred for 24 h. A yellow haze gradually formed. The solvent then was removed under vacuum, and recrystallization with hexane afforded a white solid. Yield: 0.626 g (66%). Anal. Calcd for C$_{46}$H$_{84}$Mg$_4$O$_{14}$: C 57.65, H 8.83. Found: C 57.75, H 8.78. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.12 (d, Ar−H, 4H, J = 7.2 Hz), 6.36 (dd, Ar−H, 2H, J = 7.2 Hz), 3.9−3.78 (m, OCH$_2$−, 12H), 3.72−3.64 (m, −CH$_2$−OCH$_3$, 12H), 3.4 (s, −CH$_2$−OCH$_3$, 18H), 1.48 (s, C(CH$_3$)$_3$, 18H), 1.45 (s, C(CH$_3$)$_3$, 18H); ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) 137.54 (Ar), 125.3 (Ar), 124.27 (Ar), 110.5 (Ar), 75.00 (−CH$_2$O), 75.68 (−CH$_2$O), 60.30 (−CH$_2$−OCH$_3$), 58.96 (−CH$_2$−OCH$_3$), 57.99 (−OCH$_3$), 35.31 (−C(CH$_3$)$_3$), 30.78 (−C(CH$_3$)$_3$).

Synthesis of Complex 5. A mixture of Mg^{n}Bu$_2$ (5.1 mL, 5.1 mmol), 2-methoxyethanol (0.6 mL, 7.5 mmol), and 2,6-diisopropylphenol (0.445 g, 2.5 mmol) in toluene was stirred at 0 °C for 1 h. Next, the solution was heated to 60 °C and stirred for 24 h. A pale haze gradually formed. The solvent then was removed under vacuum, and recrystallization with hexane

afforded a white solid. Yield: 0.445 g (51%). Anal. Calcd for $C_{42}H_{76}Mg_4O_{14}$: C 55.91, H 8.49. Found: C 56.06, H 8.52. ^1H NMR (300 MHz, CDCl$_3$): δ (ppm) 6.97 (d, Ar−H, 4H, J = 7.2 Hz), 6.48 (dd, Ar−H, 2H, J = 7.2 Hz), 3.81−3.72 (m, OCH_2−, 12H), 3.67−3.60 (m, −CH(CH$_3$)$_2$, 4H), 3.58−3.52 (m, −CH_2−OCH$_3$, 12H), 3.48 (s, −OCH_3, 18H), 1.21 (d, CH(CH_3)$_2$, 24H, J = 6 Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) 159.46 (Ar), 134.84 (Ar), 121.14 (Ar), 110.2 (Ar), 75.57 (−CH$_2$O), 75.23 (−CH$_2$O), 74.17 (−CH$_2$O), 59.33 (−CH$_2$−OCH$_3$), 57.95 (−CH$_2$−OCH$_3$), 57.42 (−OCH$_3$), 24.97 (−CH(CH$_3$)$_2$), 22.89 (−CH(CH$_3$)$_2$).

Polymerization of L-lactide. A typical polymerization procedure is exemplified by the synthesis of PLLA at room temperature. Unless specified otherwise, **2** (10^{-2} mmol) was added to solutions of the desired equivalent of the monomer in solvent (10 mL). The reaction was stirred at the desired temperature for the desired reaction time. After a small sample of the crude material was removed for characterization by ^1H NMR spectroscopy, the reaction was quenched with distilled water (1 drop), the solution was concentrated under vacuum, and the polymer was dissolved in dichloromethane and precipitated with excess hexane. Then, the polymer was dried under vacuum to a constant weight. The number molecular weights and polydispersity indexes (PDI) were determined by gel permeation chromatography (GPC).

Crystallographic Studies. The data were collected at low temperature (100−200 K) on SuperNova (Dual) X-ray diffraction diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods of Siemens SHELXTL PLUS program.[19] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All H atoms were placed by geometrical considerations and were added to the structure factor calculation.

ASSOCIATED CONTENT

Supporting Information
CIF files giving crystallographic data for **1**, **2**, **3**, **4**, and **5** (CCDC Reference Nos. 942413, 942414, 942415, 942416, and 942417, respectively) are available. A PDF file showing the relationship between $\ln([LA]_0/[LA]_t)$ versus time for complex **3**, $\ln k_{obs}$ versus $\ln[3]_0$ for the polymerization of L-lactide with complex **3**, $\ln([LA]_0/[LA]_t)$ versus time for complex **5**, and $\ln k_{obs}$ versus $\ln[5]_0$ for the polymerization of L-lactide with complex **5** is also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Tel.: 86 931 8912580. Fax: 86 931 8912582. E-mail: wujc@lzu.edu.cn.

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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